AD-751 629

THE TRAP STRUCTURE OF PYROLYTIC A1203 IN MOS CAPACITORS

E. Harari, et al

Princeton University

Prepared for:

Office of Naval Research

15 November 1972

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AD 751629

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) Solid State and Materials Laboratory School of Engineering and Applied Science Princeton University, Princeton, N.J. 08540	2a REPORT SECURITY CLASSIFICATION U 2b GROUP

3 REPORT TITLE

THE TRAP STRUCTURE OF PYROLYTIC Al_2O_3 in MOS CAPACITORS

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Technical Report

5 AUTHOR(S) (Last name, first name, initial)

Harari, E. Royce, B.S.H.

6. REPORT DATE 15th November 1972	7a TOTAL NO OF PAGES 9	7b NO. OF REFS 5
8a CONTRACT OR GRANT NO N00014-67-Z-0151-0026 b. PROJECT NO c. d	9a ORIGINATOR'S REPORT NUMBER(S) PSSL 141172 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10 AVAILABILITY/LIMITATION NOTICES

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11. SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY Office of Naval Research

13 ABSTRACT

The trap structure of the pyrolytic Al_2O_3 layer of MOS capacitors was investigated by a technique in which the capacitor was used as an integral detector of the charge trapped in the oxide. In all the samples studied, five trap levels were found to exist extending from 2.2 eV to 4.5 eV below the oxide conduction band. The spatial distribution of these traps was inferred from complementary photoconductivity measurements. This method is applicable to the study of the effects of radiation damage and ion implantation on the trap structure of this and other thin film insulators.

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THE TRAP STRUCTURE OF PYROLYTIC Al_2O_3 IN MOS CAPACITORS*

E. Harari and B.S.H. Royce
Solid State and Materials Laboratory
Princeton University
Princeton, New Jersey
08540

ABSTRACT

The trap structure of the pyrolytic Al_2O_3 layer of MOS capacitors was investigated by a technique in which the capacitor was used as an integral detector of the charge trapped in the oxide. In all the samples studied, five trap levels were found to exist extending from 2.2 eV to 4.5 eV below the oxide conduction band. The spatial distribution of these traps was inferred from complementary photoconductivity measurements. This method is applicable to the study of the effects of radiation damage and ion implantation on the trap structure of this and other thin film insulators.

* Work partially supported by ONR.

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Recent measurements[1,2] have shown that MOS devices with a pyrolytic Al_2O_3 gate insulator are more radiation resistant than those with a thermal SiO_2 insulator. At gate fields greater than $1.5x10^6$ volts cm^{-1}, however, they become electrically unstable even in the absence of radiation, a behavior not exhibited by devices with SiO_2 as an insulator. It has been suggested[3] that both the radiation hardness and the bias stress instability are related to charge injection and trapping in the oxide. Bias-temperature stress tests and charge measurements[4] have shown that electron traps are present in Al_2O_3 between 2.3 and 2.8 eV below the conduction band level. Balk and Stephany[5] have postulated an additional trap level at 1.0 eV below the conduction band.

This paper is concerned with a photon probe technique by which the energy, density and spatial distribution of trap levels in Al_2O_3 were directly determined. The results were reproducible for samples from three batches prepared at different times and with oxide thicknesses ranging between 800 and 1030 Å. Al_2O_3 films were deposited on 1 ohm-cm "p"-type silicon by the pyrolysis of $AlCl_3$ in a CO_2-H_2 atmosphere at 850°C[6]. Semi-transparent gold and aluminum electrodes of various geometries were filament evaporated onto the oxide and made contact with thicker, opaque electrodes to which electrical connections were made. The resulting MOS capacitors all had initial flat band voltage between zero and two volts as determined from the C-V curves[7]. All measurements were made with the samples in the vacuum environment of a dewar with liquid nitrogen temperature capability.

Electrons were photoinjected into the oxide from the inverted silicon surface by illuminating through the semi-transparent gate electrode with 5.0 eV photons while maintaining a positive gate field of 3×10^6 volts cm^{-1}. This illumination under bias was continued until the positive shift in the flat-band voltage saturated. At this point it was assumed that most of the electron traps in the oxide were filled. At 90K, devices with a gold gate electrode exhibited a flat-band shift of +20 volts at saturation and those with aluminum electrodes a shift of circa +26 volts. At the same gate field <u>in the dark</u> a shift of only +6 volts was observed. Preliminary internal photoemission measurements indicate the existance of a thin layer of SiO_2 at the Silicon-Al_2O_3 interface, the presence of which reduces charge injection in the dark. When the oxide traps had been filled to saturation at 90K, photons with energies increasing in steps of circa 0.2 eV from 1 to 5 eV were used to detrap electrons from the oxide. A negative bias field of 1.2×10^6 volts cm^{-1} was applied during these illuminations. Detrapping also occurred with a positive gate field, but for this polarity electrons were photoinjected into the oxide from the silicon and tended to refill the newly emptied traps.

In order to determine the total charge released with photons of a given energy, the dark current through the oxide was allowed to stabilize at the appropriate bias before the illumination started. The gate was then illuminated and the current arising from the emptying of traps was measured as a function of time. The illumination was continued until the photon induced current had decayed to circa the dark current value. The area under the current-time curve measured the total charge released from the traps accessible to the photons. Experiments in which the illumination was interrupted for several minutes indicated that the current decay arise solely from the emptying of trapped charge since on reillumination the current returned to the value it had had prior to the interruption rather than to some higher value. After the charge accessible to photons of a given energy had been completely removed from the oxide, a C-V plot was made to determine the corresponding negative shift in the flat band voltage. In Fig.1 plots of both $(\Delta V/\Delta E)$ and $(\Delta Q/\Delta E)$ are presented as a function of the photon energy E, where ΔE represents the incremental change in photon energy corresponding to the specific charge release. The large errors shown for ΔQ are due to uncertainties in the current level corresponding to the complete emptying of a given trap. The insert in the figure shows $(\Delta V/\Delta E)$ obtained with higher resolution on samples from other batches. Only the peaks A and B are shown but each of the five trap levels (labeled A-through E) between 2.2 and 4.5 eV were found in all three samples. Small shifts in peak energy and charge density occur from sample to sample and this may be due either to the different electrode materials employed or to the different thicknesses of the oxide layers. For a given sample the $(\Delta Q/\Delta E)$ peaks closely follow the energy positions of the $(\Delta V/\Delta E)$ peaks. The only evidence for the existence of traps at energies less than 2.2 eV is that the saturated shift in the flat band voltage at 90K is approximately 15% greater than at room temperature.

In order to ascertain the effects of the spatial location of trapped charge, the ratio:

$$(\Delta Q/\Delta V) = -\, x_o c_o \int_o^{x_o} \rho(x)dx \Big/ \int_o^{x_o} \rho(x)(x/x_o)dx \qquad (1)$$

was evaluated for various possible forms of $\rho(x)$, where C_o is the oxide capacitance, $\rho(x)$ is the charge density in the oxide, the origin of the coordinate system being at the metal-oxide interface, $x=x_o$ at the silicon-oxide interface. For $\rho(x)$ corresponding to a constant charge at $x=x_o$, $(\Delta Q/\Delta V)= -C_o$; for a uniform charge distribution through the oxide the corresponding value is $-2C_o$ and for a $\rho(x)$ decreasing linearly to zero from $x=x_o$ to $x=o$, $-3C_o/2$. With a fixed charge near the metal-insulator interface $(\Delta Q/\Delta V)>> C_o$. For the peaks A through E the $(\Delta Q/\Delta V)$ values were found to be in good agreement for samples of different C_o, oxide thickness and gate material, having the values $(0.65\pm0.1)\ C_o$, $(1.14\pm0.1)\ C_o$, $(1.21\pm0.15)C_o$, $(1.26\pm0.20)\ C_o$ and $(3.8\pm0.8)\ C_o$ respectively. These values indicate that, within the experimental error, traps B and C are at or near the silicon interface and level D is more spatially extended in the oxide. The value of $(\Delta Q/\Delta V)$ obtained for level A is not consistent with Eq.(1) and may be associated with the complex structure of the $Si-SiO_2-Al_2O_3$ interface. A trap of the same energy has been reported(8) in thermally grown SiO_2. Level E is consistent with electrons being trapped near the oxide-metal interface. However, optical absorption measurements made in this laboratory on similarly prepared Al_2O_3 films indicate a band gap of circa 8.7 eV. The energy associated with peak E is, therefore, seen to be approximately at mid gap for the oxide and photons of energy large enough to depopulate this level can also excite carriers to this level from the Al_2O_3 valence band. The free holes created in this way would contribute to ΔQ but not to ΔV. This fact prevents the above technique from being used to investigate trap distributions for levels deeper than circa 4.5 eV. Figure 2 summarizes the proposed model for the energy and spatial distribution of traps in these MOS systems. It is of interest to note that optical absorption peaks corresponding closely in energy to levels A, C and D have been reported(9,10,11) in neutron irradiated sapphire. Measurements are currently in progress to determine the atomic nature and capture cross sections of the five trap levels and the effect of oxide trapping on the radiation hardness and the threshold for internal photoemission.

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FIGURE CAPTIONS

Fig.1 Spectral distribution of oxide traps measured from the oxide conduction band energy level. ―――――――― $(\Delta V/\Delta E)$. - - - - - - - - - - $(\Delta Q/\Delta E)$ for sample #1. Samples #1,2 have gold electrodes and sample #3 an aluminum electrode. Oxide thicknesses are t_1=830 Å, t_2=1030 Å and t_3 =930 Å.

Fig.2 Band model of the MOS system to show energy and approximate spatial distribution of oxide traps. Energies given in eV. Those for the Metal-SiO_2 interface are taken from reference (12).

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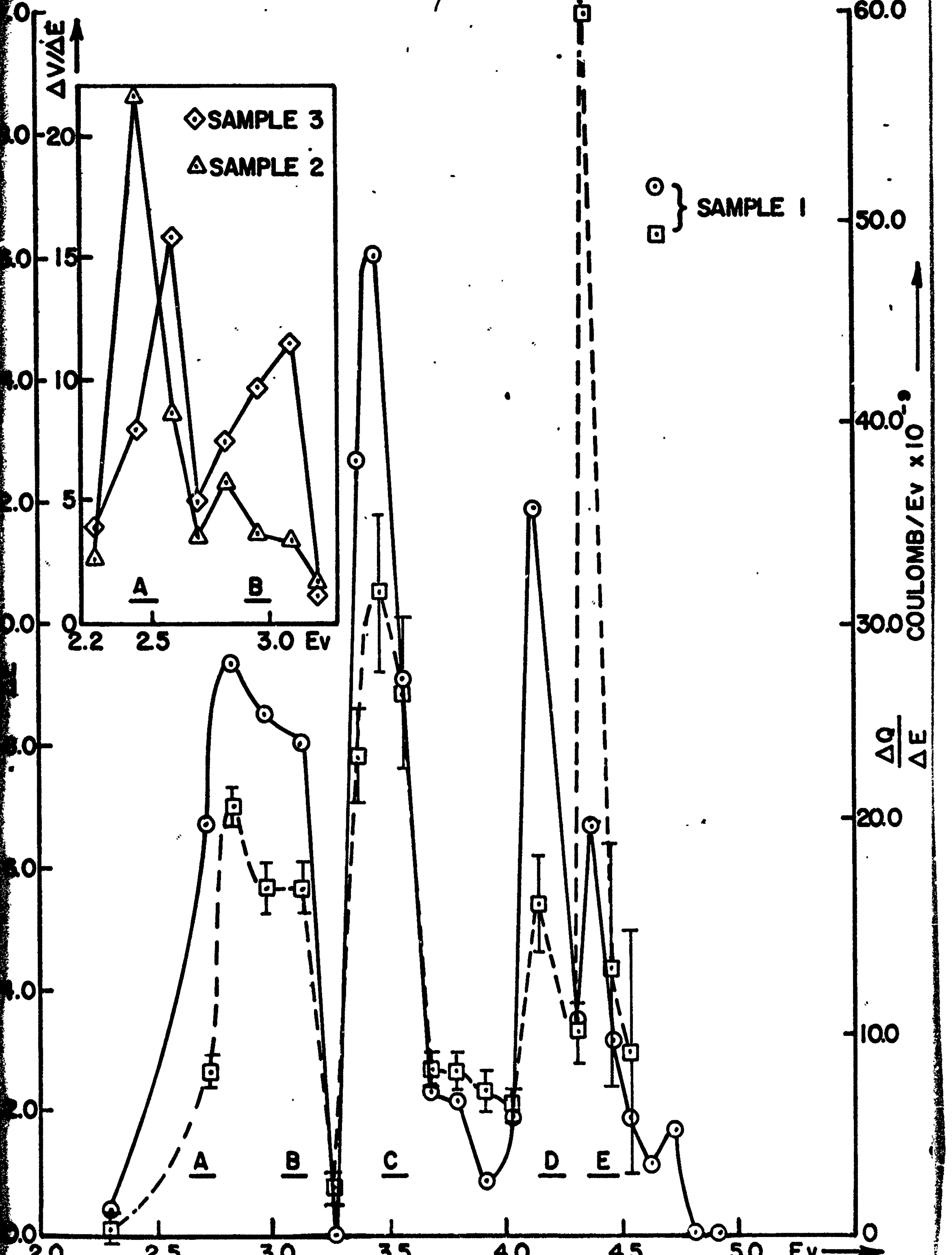
ΔV/ΔE
SAMPLE 3
SAMPLE 2
A
B
2.2
2.5
3.0 Ev
SAMPLE 1
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D
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ΔQ/ΔE
2.0
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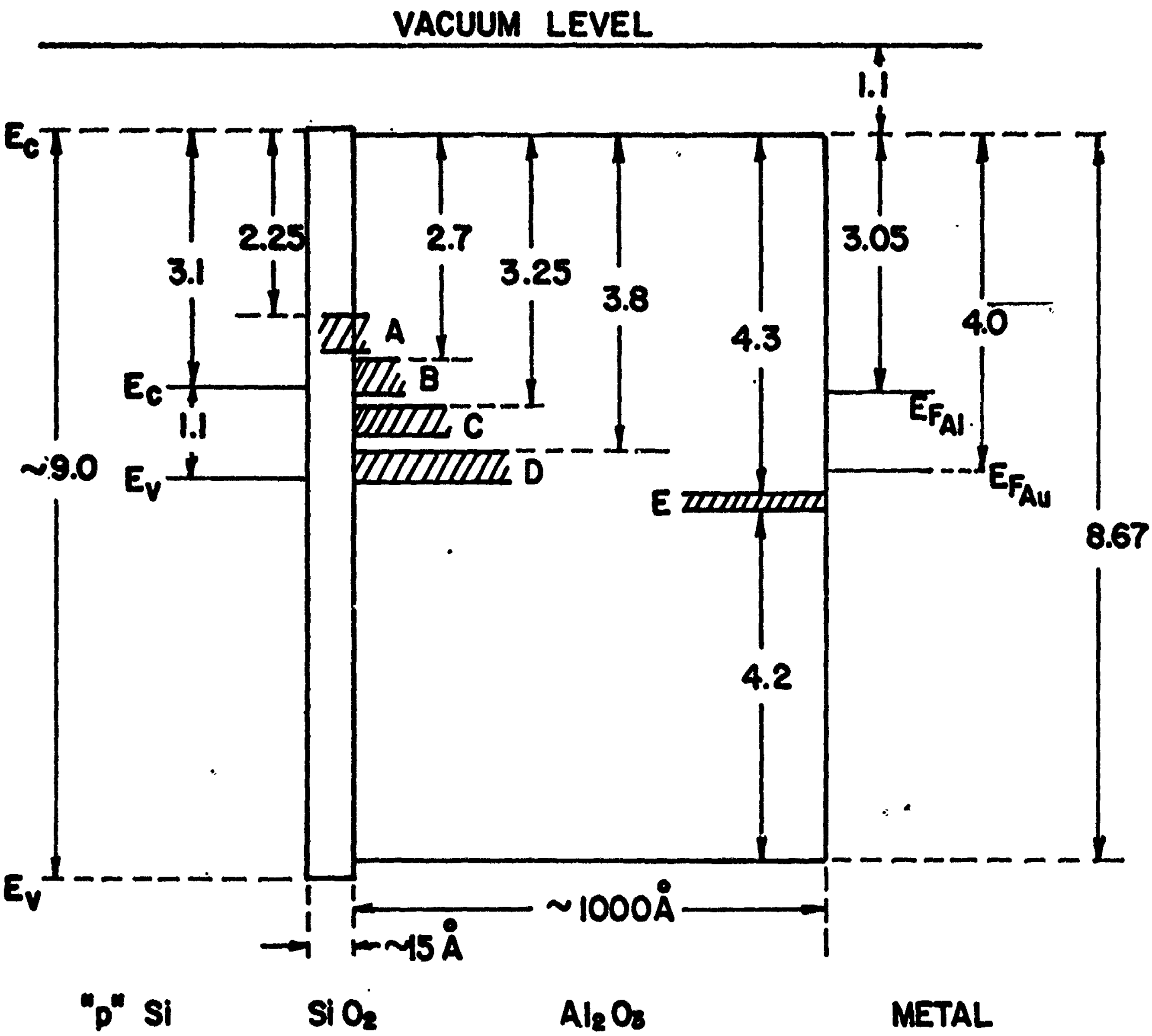

VACUUM LEVEL
1.1
E_c
3.1
2.25
2.7
3.25
3.8
4.3
3.05
4.0
A
B
C
D
E
E_c
1.1
E_v
~9.0
$E_{F_{Al}}$
$E_{F_{Au}}$
8.67
4.2
E_v
~1000 Å
~15 Å
"p" Si
SiO_2
Al_2O_3
METAL